Magnetic structure of dilute ferrite $Ni_{0.2}Zn_{0.8}Fe_2O_4$

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It is shown that, due to the competition between antiferromagnetic and ferromagnetic exchange reactions, the ferrite $Ni_{0.2}Zn_{0.8}Fe_2O_4$ exhibits a frustrated magnetic structure consisting of separate spontaneously magnetized domains in which the ferromagnetic order is predominant (sperimagnetism).

1. Magnetic materials with frustrated magnetic structure are attracting considerable attention. Their magnetic state below the spin ordering temperature T_C is determined by the balance of exchange interactions at each lattice site occupied by a magnetic ion.

Materials with frustrated magnetic structure occupy an intermediate position between ordinary magnets and spin glasses. They have some features in common with spin glasses, but they are closer to the results of theories developed for ordinary magnets with long-range magnetic order. According to Ref. 1, frustrated magnetic structure can be observed in magnetic materials consisting of two or more types of magnetic ions. For $T < T_C$, these materials contain a net of spontaneously magnetized regions dominated by ferro-, antiferro- or ferrimagnetic order. Such compounds with frustrated magnetic structure are called spero-, aspero-, and sperimagnets.

According to the Goodenough-Kanamori rules,[2–4] indirect exchange interactions have the following signs in a dilute ferrite with the composition $Zn^{2+}_{0,8}FE^{3+}_{0,2}[Ni^{2+}_{0,2}Fe^{3+}_{1,8}]O_4$,

intersublattice *AB*-interactions:

$Fe_A^{3+}-O^{2-}-Fe_B^{3+}<0$, $Fe_A^{3+}-O^{2-}-Ni_B^{2+}<0$,

intrasublattice *BB*-interactions

$Fe_B^{3+}-O^{2-}-Fe_B^{3+}<0$, $Ni_B^{2+}-O^{2-}-Fe_B^{3+}>0$,

intrasublattice *AA*-interactions

$Fe_A^{3+}-O^{2-}-Fe_A^{3+}<0$.

In undiluted ferrites with spinel structure, indirect interactions follow the following order:

$$|J_{AB}| \gg |J_{BB}| > |J_{AA}|,$$

whereas in a ferrite of this composition

$$|J_{BB}| > |J_{AB}| \gg |J_{AA}|,$$

since its *A*-sublattice contains a small amount of the magnetic cations Fe^{3+}. Since in ferrites with spinel structure the *AA*-interactions are always small (and even smaller in our ferrite), the interaction $Fe_A^{3+} - O^{2-} - Fe_A^{3+} < 0$ will not be taken into account in our calculations. Consequently, in the ferrite $Ni_{0,2}Zn_{0,8}Fe_2O_4$ the intrasublattice negative exchange interaction $Fe_B^{3+} - O^{2-} - Fe_B^{3+}$ will be the dominant interaction, and the positive $Ni_B^{2+} - O^{2-} - Fe_B^{3+}$ and negative $Fe_A^{3+} - O^{2-} - Fe_B^{3+}$ exchanges will act against it. It follows that the conditions necessary for the appearance of frustrated magnetic structure will obtain in this material. To verify this conclusion, we must examine in detail the behavior of a number of magnetic properties of this ferrite and compare them with the analogous properties of ferrites with unfrustrated magnetic structure and with spin glasses.

2. A specimen of the ferrite $Ni_{0,2}Zn_{0,8}Fe_2O_4$ was prepared by the ceramic method. X-ray analysis showed that the specimen contained a single phase. Measurements were then performed of the temperature dependence of the magnetization σ (by the ballistic method) and of the magnetocaloric effect ΔT.

3. Figure 1 shows the magnetization isothermals $\sigma(H)$ for the $Ni_{0,2}Zn_{0,8}Fe_2O_4$ specimen under investigation. It is clear that, for fields up to 10 kOe, the $\sigma(H)$ isothermals do not saturate even at 4.2 K. This is unrelated to the overcoming of magnetic anisotropy forces because all the magnetic cations in this ferrite are orbital singlets in the ground state, so that their contribution to magnetic anisotropy is small. Since the function $\sigma(H)$ is nonlinear in strong fields , it is difficult to determine the spontaneous magnetization by simple extrapolation. This type of $\sigma(H)$ isothermal is observed in the region of the Curie point of undiluted magnetic materials in which the rise in magnetization in strong fields (paraprocess) is due to the rotation of the magnetic moments of correlated regions. We consider that the observed shape of the $\sigma(H)$ curve may be regarded as confirmation of our conclusion that the magnetic structure of the dilute ferrite $Ni_{0,2}Zn_{0,8}Fe_2O_4$ consists of individual spontaneously-magnetized regions.

Figure 2 reproduces the temperature dependence of magnetization $\sigma(T)$, determined in low fields H. It is clear that the magnetic ordering temperature of the ferrite

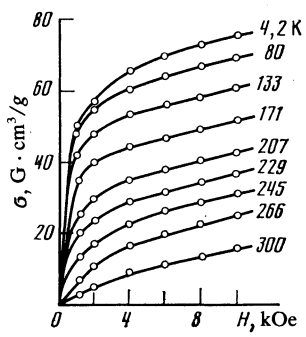

FIG. 1. Isothermals of specific magnetization $\sigma(H)$ of the $Ni_{0,2}Zn_{0,8}\cdot Fe_2O_4$ specimen.

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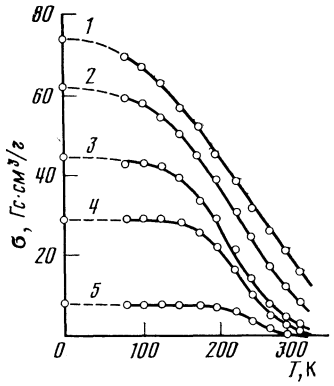

FIG. 2. Temperature dependence of the magnetization of the ferrite $Ni_{0,2}Zn_{0,8}Fe_2O_4$ in different fields: 1—$H = 10$ kOe; 2—$H = 6$ kOe; 3—$H = 2$ kOe; 4—$H = 1$ kOe; 5—$H = 0.25$ kOe.

$Ni_{0,2}Zn_{0,8}Fe_2O_4$ is difficult to determine because the external magnetic field substantially delays the disordering of the spontaneously-magnetized regions. The considerable stability of frustrated magnetic structure in an external magnetic field appears to be one of its characteristic features.

We have used the method of thermodynamic coefficients[5] to determine the magnetic ordering temperature T_C and the spontaneous magnetization σ_s of the ferrite $Ni_{0,2}Zn_{0,8}Fe_2O_4$. It is well-known that the magnetization σ is described by the following equation in the region of the Curie temperature:

$$\alpha+\beta\sigma^2=H/\sigma,$$

where α and β are the thermodynamic coefficients that depend on T and P, $\sigma = \sigma_i + \sigma_s$, σ_i is the specific magnetization of the paraprocess (true magnetization), and σ_s is the specific spontaneous magnetization.

The coefficient α is positive above and negative below the Curie point T_C and vanished at $T = T_C$; the coefficient β is always positive.

We have found that, in contrast to undiluted ferro- and ferrimagnets, our specimen exhibited a linear dependence of H/σ on σ^2 not only near the Curie point, but in a broader temperature range, i.e., the behavior was similar to that of magnetic materials with spin-glass type ordering. It is clear from Fig. 3 that the transition temperature T_C from the paramagnetic state to the ordered state is about 245 K for this dilute ferrite.

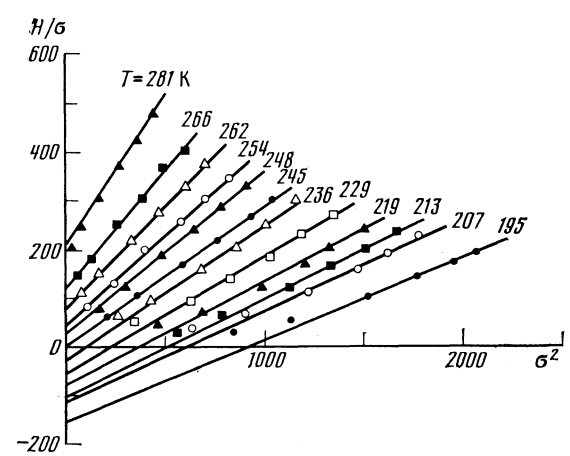

FIG. 3. The dependence of H/σ on σ^2 for the $Ni_{0,2}Zn_{0,8}Fe_2O_4$ specimen.

We suggest that, in materials with frustrated magnetic structure, the paraprocess in the region of T_C is due to not only the rotation of magnetic moments of spontaneously magnetized regions, but also the increase in their magnetic moments. It is probable that the effect of magnetic-field energy on the exchange interactions in these materials gives rise to (as in the case of spin glasses) a diffuse phase transition from the ordered magnetic state to the paramagnetic state.

The degree of diffuseness of this transition and the magnitude of the paraprocess can be judged from the temperature dependence of the differential susceptibility $|\chi_{diff}|_{H=const}(T - T_c)$ of the paraprocess. Direct measurements of χ_{diff} of magnetic materials with low magnetization are quite difficult. However, it follows from Ref. 6 that, if we know the thermodynamic coefficients α and β and the magnetization σ in a particular field H, we can calculate χ_{diff} for any temperature from the formula

$$|\chi_{diff}|_{H=const}=1/(\alpha+3\beta\sigma^2)$$

and hence find its temperature dependence in the region of the ordering temperature. Figure 4 shows the temperature dependence of $|\chi_{diff}|_{H=1\,kOe}(T - T_c)$ for the ferrite $Ni_{0,2}Zn_{0,8}Fe_2O_4$(Ni − Zn). For comparison, we also show the corresponding curves taken from Ref. 6 for the ferrites $Mg_{1,5}Ti_{0,5}FeO_4$(Mg − Ti) (spin-glass type structure) and $Li_{0,2}Zn_{0,6}Fe_{2,2}O_4$(Li − Zn) (long-range ferrimagnetic order). It is clear that, as we have suggested, the differential susceptibility χ_{diff} of the paraprocess at $T = T_C$ in the Ni-Zn ferrite is not only much greater than the value of χ_{diff} in the Mg-Ti ferrite, but is greater by a factor of almost two as compared with the Li-Zn ferrite. As far as the diffuseness of the phase transition is concerned, the phase transition from the ordered to the paramagnetic state occupies a broader temperature interval in the Ni-Zn and Mg-Ti ferrites than in the Li-Zn ferrite.

Thus, a substantial paraprocess in the temperature region near T_C is one of the essential indicators of the presence

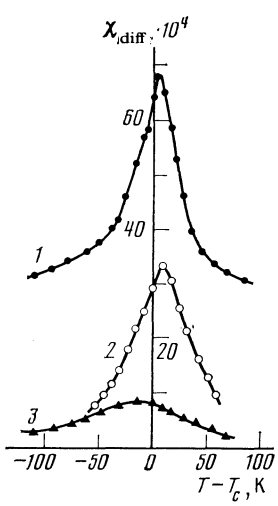

FIG. 4. Temperature dependence of χ_{diff} for different coumpounds: 1—$Ni_{0,2}Zn_{0,8}Fe_2O_4$; 2—$Li_{0,2}Zn_{0,6}Fe_{2,2}O_4$; 3—$Mg_{1,5}Ti_{0,5}FeO_4$.

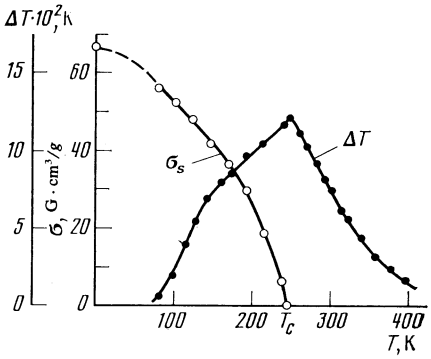

FIG. 5. Temperature dependence of spontaneous magnetization σ_s and the magnetocaloric effect ΔT for $Ni_{0,2}Zn_{0,8}Fe_2O_4$.

of frustrated magnetic structure in the material.

In ferro- and ferrimagnetis with long-range magnetic order, rotation of the magnetic moments of correlated regions in an external magnetic field at temperatures near the Curie point leads to a change in the temperature of the specimen (this is the magnetocaloric effect ΔT). Hence it follows that, if the magnetic structure of the material consists of individual spontaneously-magnetized regions, studies of the behavior of the magnetocaloric effect should yield useful information.

We have therefore carried out measurements of the ΔT-effect on the $Ni_{0,2}Zn_{0,8}Fe_2O_4$ specimen. It is clear from Fig. 5 that the effect exhibits a broad maximum occupying a temperature interval of about 300 K whilst, in ordinary magnets, this figure is lower by almost an order of magnitude. We have found no reference in the literature to this type of anomalous behavior of the ΔT-effect. It is interesting to note that the peak on the $\Delta T(T)$ curve occurs in the region of 245 K, i.e., it coincides with the temperature T_C determined above by the method of thermodynamic coefficients. Our data on the magnetocaloric effect also support the conclusion that the magnetic structure of the $Ni_{0,2}Zn_{0,8}Fe_2O_4$ specimen consists of individual spontaneously magnetized regions.

We have used the graphs of H/σ against σ^2 to determine the spontaneous magnetization σ_s and have constructed the function

$$\lg(\sigma_s/\sigma_{s_0}) = f \lg(T/T_C),$$

(σ_{s0} is the spontaneous magnetization at 0 K). We have found that $f = 1/2$, i.e., as the Curie point is approached, spontaneous magnetization follows the same law as for ordinary ferro- and ferrimagnets, i.e.,

$$\sigma_s/\sigma_{s_0} = \xi(1-T/T_C)^{1/2}.$$

[1]J. M. D. Coey, J. Appl. Phys. **49**, 1646 (1978).
[2]J. B. Goodenough, Magnetism and the Chemical Bond, Wiley, 1963 [Russ. translation, Metallurgiya, Moscow, 1968].
[3]J. B. Goodenough and A. H. Loeb, Phys. Rev. **98**, 391 (1955).
[4]J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959).
[5]K. P. Belov and A. N. Goryaga, Fiz. Met. Metalloved. **2**, 4 (1956).
[6]K. P. Belov, A. N. Goryaga, and A. I. Kokorev, Vestn. Mosk. Univ. Fiz. Astron. Ser. 3, **21**, 69 (1980).

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